

Metal-Nicotine Double Sulfates

BY CLAUDE R. SMITH

The inorganic double sulfates represented by the formula $R_2M(SO_4)_2 \cdot 6H_2O$, where R is an alkali metal, thallium or ammonium, and M is Cu, Mg, Zn, Fe, Co, Ni, Mn or Cd constitute an important isomorphous group of compounds. Although slight variations in crystal measurements and other physical properties occur, they appear to be largely determined by some property of the univalent R-metal or radical rather than the specific M-metal.

The metal-nicotine double sulfates described here contain the bivalent cations of the M-metals and also the trivalent cations of Fe, Cr and Al. No similar group of double sulfates containing nicotine or other organic base has been reported previously. This study forms part of an extensive investigation in this Laboratory on the coordination of nicotine in forming nicotineamine and double salt compounds.

Experimental

Compounds 1 to 7, inclusive, in Table I represent the addition of "neutral" nicotine sulfate ($2C_{10}H_{14}N_2 \cdot H_2SO_4$) to the metal sulfate. The nicotine sulfate was prepared by dissolving weighed amounts of base and acid in absolute ethanol, but adjustment was made until a drop of the solution, after dilution with water, gave an intermediate tint with methyl red indicator. Number 7, however, crystallized better if nicotine was used in sufficient excess to give a yellow tint with the indicator. "Acid" nicotine sulfate ($C_{10}H_{14}N_2 \cdot H_2SO_4$), prepared by dissolving weighed amounts of base and acid in absolute ethanol, reacted directly with the normal sulfates of nos. 8, 10 and 11, but a better procedure for no. 10 was to form the sulfato-

acid $Cr_2(SO_4)_3 \cdot 3H_2SO_4$ in ethanol-water and then add the nicotine in ethanol slowly with stirring. Number 9 also was better prepared through the sulfate-acid $Fe_2(SO_4)_3 \cdot H_2SO_4$ in ethanol-water by the addition of nicotine in ethanol.

Number 1 (representative of nos. 1 to 6, inclusive) was prepared as follows: 7.5 g. (0.03 mole) of cupric sulfate was dissolved in 20 ml. of water in a 250-ml. Erlenmeyer flask, and mixed with 100 ml. of absolute ethanol containing 0.04 mole of neutral nicotine sulfate (one-third excess). Absolute ethanol was then added in 10-ml. portions until complete precipitation of the double salt occurred. After standing for several hours (or overnight), the crystals were filtered off and washed with 95% ethanol. It was dried in air but bottled as soon as dry, for it lost hydrate water under low-humidity conditions.

For no. 7, 13.4 g. (0.06 mole) of manganous sulfate tetrahydrate was used with 0.04 mole of nicotine sulfate (prepared as indicated above).

Number 8 was prepared by dissolving 0.03 mole of magnesium sulfate heptahydrate in 12 ml. of water (with gentle warming), and adding 0.04 mole of acid nicotine sulfate in 100 ml. of absolute ethanol. Absolute ethanol was then added in 10-ml. portions until a suspension of the crystals was formed. After standing, the crystals were filtered off and washed with absolute ethanol. It was dried to constant weight in a desiccator with renewed amounts (a few grams) of calcium chloride. If properly prepared, it was not appreciably hygroscopic.

Number 9 was prepared from Monsel's salt, $Fe_4(SO_4)_5 \cdot (OH)_2 \cdot 10H_2O$, following the equation $Fe_4(SO_4)_5 \cdot (OH)_2 + 3H_2SO_4 + 4C_{10}H_{14}N_2 \rightarrow 2[Fe_2(SO_4)_3 \cdot 2C_{10}H_{14}N_2 \cdot H_2SO_4 \cdot 6H_2O] + xH_2O$, except that $4H_2SO_4 + 6C_{10}H_{14}N_2$ was used to provide an excess of neutral nicotine sulfate. Probably a better procedure is to dissolve 9.2 g. of Monsel's salt (mol. wt., 917.8) in a 100-ml. solution composed of 80 ml. of ethanol and 20 ml. of water containing sulfuric acid (0.04 mole) and then add 0.06 mole of nicotine in 100 ml. of ethanol. If required for a good crystal suspension, more ethanol is added.

It was dried in the same way as No. 8. It was kept in a closed container in a desiccator containing calcium chloride because it was deliquescent.

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TABLE I
METAL-NICOTINE DOUBLE SULFATES

No.	Compound	Nicotine, %		SO ₄ , %		Metal, %		H ₂ O, %		Color
		Found	Calcd.	Found	Calcd.	Found	Calcd.	Difference	Calcd.	
1	CuSO ₄ ·2RN ₂ ·H ₂ SO ₄ ·8H ₂ O ^a	44.4	44.7	27.1	26.5	8.9	8.8	19.3	19.8	Blue
2	CoSO ₄ ·2RN ₂ ·H ₂ SO ₄ ·8H ₂ O ^a	44.4	44.9	27.6	26.6	19.5	20.0	Red
3	FeSO ₄ ·2RN ₂ ·H ₂ SO ₄ ·8H ₂ O ^a	44.5	45.1	27.6	26.7	7.9	7.6	19.7	20.1	Yellow
4	ZnSO ₄ ·2RN ₂ ·H ₂ SO ₄ ·8H ₂ O ^a	42.8	44.5	27.6	26.4	9.4	9.0	20.0	19.7	White
5	CdSO ₄ ·2RN ₂ ·H ₂ SO ₄ ·8H ₂ O ^a	41.4	41.9	25.6	24.8	White
6	NiSO ₄ ·2RN ₂ ·H ₂ SO ₄ ·9H ₂ O	43.1	43.9	26.7	26.0	7.8	7.7	22.0	21.9	Blue
7	2MnSO ₄ ·2RN ₂ ·H ₂ SO ₄ ·11H ₂ O	34.9	35.1	32.2	31.2	11.9	11.9	20.7	21.5	White
8	MgSO ₄ ·RN ₂ ·H ₂ SO ₄ ·6H ₂ O	32.4	33.2	40.5	39.3	5.3	5.0	21.3	22.1	White
9	Fe ₂ (SO ₄) ₃ ·2RN ₂ ·H ₂ SO ₄ ·6H ₂ O	34.6	34.9	40.8	41.3	11.2	12.0	13.2	11.6	Maroon
10	Cr ₂ (SO ₄) ₃ ·3RN ₂ ·3H ₂ SO ₄ ·6H ₂ O	38.0	38.0	42.8 ^b	44.9	8.4	8.1	8.2	8.4	Green
11	Al ₂ (SO ₄) ₃ ·2RN ₂ ·2H ₂ SO ₄ ·14H ₂ O	29.0	29.1	42.9	43.1	5.6	4.9	22.1	22.6	White

^a RN₂ is an abbreviation of C₁₀H₁₄N₂. ^b SO₄ contaminated the Cr(OH)₃ removed before estimation.

Number 10 was prepared by the following method: A 25-ml. aliquot of a chromic sulfate solution (anal., 0.728 g. chromic oxide) was mixed with 4 g. of sulfuric acid and evaporated to about 10 ml. on the steam-bath. The 10-ml. solution was diluted with 100 ml. of absolute ethanol, and to it was added, in small portions, 100 ml. of absolute ethanol containing 7 g. of nicotine, with stirring after each addition. The hard gray-green crystals formed did not adhere to the Erlenmeyer flask, and after standing overnight were filtered and dried. It was kept dry in the same manner as No. 9.

Number 11 was prepared by dissolving 13.4 g. (0.02 mole) of Al₂(SO₄)₃·18H₂O in 10 ml. of water and adding 0.06 mole each of nicotine and sulfuric acid dissolved in 150 ml. of methanol. After several days, a good suspension of crystals was formed, which was filtered, washed with absolute ethanol, and dried in the same way as No. 8. A better yield was obtained by adding an equal volume of ethanol. The final product was fairly free of hygroscopicity under low-humidity conditions but was preserved in a desiccator containing calcium chloride.

Discussion

Double salts containing Cu, Co, Fe, Zn, Cd or Ni have the same type formula, MSO₄·2C₁₀H₁₄N₂·H₂SO₄·xH₂O, where x is probably 8 except with Ni, which may be 9. Uncertainty regarding x results in part from irregularities in composition best shown by the weight ratio SO₄:C₁₀H₁₄N₂, which should be 0.592:1. The metal content is probably too high, but errors in analysis and variations in water content render this criterion less useful. Number 4, which contains Zn, has the greatest deviation in the ratio SO₄:C₁₀H₁₄N₂, which is 0.641:1. On evaporation, its saturated water solution deposited two kinds of crystals. The first might have been ZnSO₄·7H₂O, but later a uniform deposition of the double salt took place because nicotine sulfate was then in excess. Number 1 is probably the purest double salt of the group, with SO₄:C₁₀H₁₄N₂ in a ratio of 0.612:1, although its water content may vary because of humidity conditions. When dried over sulfuric acid, No. 1 lost 19.75% H₂O; there was no further loss at 110°; H₂O by difference was 19.8%. In dry weather No. 1 may lose about 6 moles of water, changing from medium blue to dark blue, but the color is not so dark as that of the anhydrous compound. After

several days' drying over sulfuric acid, all other double salts lost only about 6 moles of water. Number 3 was light yellow and quite stable in the dry state, but some oxidation occurred during preparation. The lightest colored crystals were obtained by dissolving powdered FeSO₄·7H₂O in a nicotine sulfate-water solution (containing the proper amount of water) and promptly precipitating with ethanol. A two-phase liquid was first formed, which later separated into a suspension of the double salt in the ethanol-water solution. Two-phase liquids were usually formed with all the metals except copper and cobalt.

Number 11 was the only double sulfate in which the use of methanol appeared to be advantageous. This solvent readily dissolved Nos. 1 to 8, inclusive, and appeared unsatisfactory for their preparation. It dissolved No. 11 with difficulty, but the subsequent addition of ethanol increased yields without causing deterioration of the final product.

Each metal sulfate combines with only one nicotine sulfate, either "acid" or "neutral." Crystals were obtained by evaporation of saturated aqueous solutions of the compounds. Those with Co, Ni, Zn, or bivalent Fe were similar rhombic prisms ending in sphenoids and resembling the rhombic form of MgSO₄·7H₂O; those with Cd and Cu were bipyramids and triclinic prisms, respectively; those with Mn were rectangular plates mostly stacked in piles; those with Mg were a mass of woolly needles. Compounds of the trivalent metals did not crystallize properly from water.

Preparation of all compounds except No. 11 involved a nearly complete precipitation of the metal. Yields of Nos. 1 to 8, inclusive, based on the hydrated metal sulfates, were nearly quantitative. Yields of Nos. 9 and 10 were based on analyses for metal, and were used as checks for their formulas. Double salts could not be prepared with either calcium or silver sulfate.

Summary

Metal sulfates containing bivalent cations of

either Cu, Co, Fe, Zn, Cd, Ni, Mn or Mg or trivalent cations of Fe, Cr or Al were combined with either neutral or acid nicotine sulfate to

produce hydrated double sulfates. Methods of preparation and properties are described.
PHILADELPHIA 18, PA.